

Mid- and near-infrared spectroscopic assessment of soil compositional parameters and structural indices in two Ferralsols

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Abstract

Bulk soil samples (BS) ($n=120$) from long-term tillage experiments and areas covered by secondary natural forest were collected in the Brazilian savanna region (Cerrado) at Santo Antônio de Goiás, and southern Atlantic forest region at Londrina. Bulk soils were separated into 8 aggregate size fractions (ASF) by wet sieving ($n=700$). Bulk soil samples (BS) and ASF were analyzed for total C, N by dry combustion. BS were also analyzed for sand, silt, and clay by densitometry, and several measures of soil aggregation were determined. All samples were scanned in the mid- and near-infrared (Mid-IR, NIR) by diffuse reflectance of ground, non-KBr diluted samples using a Digilab FTS-7000 FTIR spectrometer equipped with a Pike Auto-Diff auto-sampler. Quantitative calibrations for the various analytes were performed separately for the original set of 120 BS samples and the set of 700 ASF samples using partial least squares regression (PLSR). Results for the set of 120 BS for total C and N were excellent using either spectral range with $R^2 > 0.97$, except for C by Mid-IR ($R^2 = 0.93$). Similar results were obtained for determinations of sand and clay ($R^2 > 0.94$). Silt, determined by difference ($100\% - \% \text{ sand} - \% \text{ clay}$), gave much lower R^2 (0.80 and 0.63 for Mid-IR and NIR, respectively). For aggregation indices, R^2 of ~ 0.80 were achieved in the Mid-IR, NIR results were not as good ($R^2 < 0.67$). Efforts with the 700 ASF samples resulted in R^2 of 0.98 and 0.96 for C, and 0.96 and 0.97 for N, for Mid-IR and NIR calibrations, respectively. Calibration efforts to determine the values for the set of 700 ASF samples using set of 120 BS from which they were fractionated gave $R^2 = 0.90$ and 0.87 in the Mid-IR and NIR, respectively, when 5% of the ASF were added to the set of 120 BS. Spectral discrimination of sample source was easily and very accurately determined for all data sets examined.

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1. Introduction

In many research endeavors, large numbers of samples are either required or generated. These samples likely then need to be analyzed for one or more analytes of interest which is often time consuming and expensive. An important example of the need for large scale

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analyses would be soil C inventory assessments that become mandated under international climate change agreements that include accounting for soil carbon sequestration as may occur under future enforcement periods of the [Kyoto Protocol \(1997\)](#). As an effect of this, the ability to measure carbon sequestration in soils and assess the role of soil in carbon fluxes is becoming more relevant. The Conference of the Parties (COP) of the United Nations Framework Convention on Climate Change (UNFCCC) is making efforts to implement the Kyoto Protocol and to make the necessary modifications required from the International Panel on Climate Change (IPCC) on a special report on the principal aspects of an analytical procedure related to carbon ([Watson et al., 2000](#)). It is thus highly probable that there will soon be a strong demand for determination of C in soils for the evaluation of agricultural production and forestry systems in assessment of their role in global climate change mitigation. If this occurs, large numbers of samples will need to be analyzed by fast, accurate and inexpensive means. Among the presently available methods for soil carbon quantification combustion is considered sufficiently accurate ([Watson et al., 2000](#)), however, rather expensive. Loss-on-ignition and wet digestion ([Nelson and Sommers, 1996](#); [Embrapa, 1997](#)) are time consuming and require the use of harsh chemicals and are prone to bias ([Watson et al., 2000](#)).

In many areas of agriculture both commercial and research spectroscopic methods based on near-infrared reflectance spectroscopy (NIRS) have come to be used to reduce the need for chemical base and even other instrumentally based methods of sample analysis ([Williams and Norris, 1987, 2001](#); [Roberts et al., 2004](#)). In NIRS, calibrations are developed using a representative sample set to relate spectral information to the analyte in question (calibrations), for example protein in wheat ([Tkachuk, 1987](#)), using a process known as chemometrics ([Williams and Norris, 1987](#); [Beebe et al., 1998](#); [Williams and Norris, 2001](#); [Naes et al., 2002](#); [Roberts et al., 2004](#)). While NIRS has come to dominate many areas of analysis in agriculture, the analysis of soils using NIRS has only relatively recently been examined for quantitative analysis ([Reeves et al., 1999](#); [Reeves and McCarty, 2001](#); [Reeves et al., 2002](#)).

While NIRS uses electromagnetic radiation in the 25,000 to 4000 cm^{-1} (400–2500 nm) range, diffuse reflectance Fourier Transform mid-infrared (Mid-IR) spectroscopy (DRIFTS) uses radiation in the range from 4000 to 400 cm^{-1} (2500–25,000 nm). Virtually all agricultural applications using diffuse reflectance (illumination of a ground, non-mirror like sample) are based on NIRS because it was thought that quantitative

analysis using DRIFTS was impossible unless samples are diluted with KBr to a concentration of 5% or less. The dilution being needed to avoid spectral distortions caused by mirror-like reflection known as specular reflection which does not occur in the near-infrared (NIR) where absorptions are weaker ([Reeves, 2003a,b](#)). However, efforts have demonstrated that quantitative analysis can be performed using DRIFTS generated spectra in conjunction with chemometrics and they provide strong indications that DRIFTS can outperform NIRS for soils ([Reeves, 1994, 1996](#); [Janik et al., 1998](#); [Reeves et al., 2001](#); [McCarty et al., 2002](#); [Reeves et al., 2002](#)).

The objective of this work was to examine the usefulness of DRIFTS and NIRS in the quantitative determination of total carbon and nitrogen in soil samples collected under a case study assessing the mechanism of soil organic carbon accumulation in Ferralsols as affected by soil structural dynamics under traditional and conservation tillage systems and under secondary natural forest ([Madari et al., 2005a](#)). In addition, the capability of DRIFTS and NIRS was also examined in assessing the particle size distribution of the soil and the indicators that describe soil aggregate distribution as a measure of soil structural properties.

2. Materials and methods

2.1. Field sites

The tillage experiments were located in Londrina (23°23'S; 51°11'W) and Santo Antônio de Goiás (16°28'S; 49°17'W). In Londrina (southern Atlantic Forest biome), the mean annual temperature is 20.7 °C with monthly means between 11 °C in July and 31 °C in February, and annual rainfall 1622 mm, two-thirds occurring during the warm season (October to March). The soil type was a Rhodic Ferralsol [WRB ([FAO, ISRIC, ISSS, 1994](#))] or Latossolo Vermelho eutroférico according to the Brazilian Soil Classification System ([Embrapa, 1999](#)) or Rhodic Hapludox according to the USDA Soil Taxonomy ([Soil Survey Staff, 1999](#)). The dominant species at the forest site, which is at the same altitude and on the same soil type, were *Trichilia clausenii*, *Euterpe edulis* and *Andidosperma polyneuron* ([Oliveira-Filho and Ratter, 1995](#)). It is assumed that the same species characterized the site prior to forest clearance ca. 1940. The intermediate vegetation at the field site in Londrina comprised pasture grasses (*Brachiaria* spp. and *Penisetum clandestinum*) and coffee plantation. The field experiment was established in 1987. In Santo Antônio de Goiás, the mean annual

temperature is 23 °C, and annual rainfall 1500 mm. There are two distinct seasons in this Cerrado biome: the rainy season from September to May and the dry season from June to August. Cultivation of cash crops is limited to the rainy season, but dry spells in the rainy season are also common (Assad et al., 1994). The soil type was a Haplic Ferralsol (WRB) (Latossolo Vermelho-Amarelo distrófico according to the Brazilian Soil Classification System; or Typic Haplustox according to the USDA Soil Taxonomy). The Cerrado vegetation in this region is characterized by plant species, such as *Magonia pubescens*, *Dilodendrum bipinnatum* and *Hirtella glandulosa*. Forest was cleared in the 1960s and prior to the establishment of the experiment in 1995 the area was covered by *Andropogum* sp. for 6 years and lastly by maize–common beans rotation. The dominant mineral of the clay-size fraction (<2 µm) was kaolinite in both soils, the soil in Santo Antônio de Goiás showing relatively stronger signs of gibbsite and hematite. Some physico-chemical characteristics of the two soils are described in Table 1.

In Londrina, the tillage treatments were conventional tillage (disc plough at 18 cm depth followed by harrowing twice with light discs at 10 cm depth, CT) and no-tillage (no disturbance to the soil other than the sowing operation, NT). Two rotations were a crop succession (SUC) of wheat (*Triticum aestivum* L.) followed by soybean (*Glycine max* L.) and a crop rotation (ROT) including white lupine (*Lupinus albus* L.)/maize (*Zea mays* L.)–black oat (*Avena strigosa*

Schieb.)/soybean–wheat/soybean–wheat/soybean. In Santo Antônio de Goiás, the tillage treatments (main plots) were conventional tillage (mouldboard plow followed by harrowing twice with light discs, CT) and no-tillage (NT). The subplots were crop succession (SUC), which included fallow/rice (*Oriza sativa*)–fallow/soybean (*G. max*) and the rotation (ROT) with sunhemp (*Crotalaria juncea*)/rice-millet (*Pennisetum glaucum* L.R. Br.)/soybean. All plots were in triplicate.

2.2. Soil samples

Both tillage experiments were sampled in a similar way. Bulk soil samples were collected from 4 different tillage-rotation treatments. Each treatment was sampled in triplicate in the field and at 4 depths (0–5, 5–10, 10–20, 20–30 cm). In addition soil samples were similarly taken from the nearby forests (4 depths from three pits positioned 50 m apart), resulting in a total of 120 bulk soil (BS) samples [(2 areas × 4 treatments × 3 replicates × 4 depths) + (forest: 2 areas × 3 replicates × 4 depths)].

2.3. Sample preparation

Each bulk soil sample from the 0–5, 5–10, 10–20 cm sampling layer was fractionated into 8 aggregate size fractions (ASF) (8–19, 4–8, 2–4, 1–2, 0.5–1, 0.25–0.5, 0.125–0.25, 0.053–0.125 mm diameter) by wet sieving (Madari et al., 2005a) resulting in 700 ASF samples. The ASF samples were dried, and ground to pass an 80-

Table 1
Chemical properties (A) and particle size distribution (B) of the Rhodic Ferralsol, Londrina, and of the Haplic Ferralsol, Santo Antônio de Goiás

(A) Chemical properties							
	pH _{H₂O}	Al ³⁺ (cmol _c .dm ⁻³)	H + Al (cmol _c .dm ⁻³)	Ca ²⁺ (cmol _c .dm ⁻³)	Mg ²⁺ (cmol _c .dm ⁻³)	K ⁺ (cmol _c .dm ⁻³)	P _{available} (mg.kg ⁻¹)
<i>Rhodic Ferralsol (Londrina)</i>							
Forest	6.3	0.1	4.5	14.9	2.6	0.58	30
Experiment	5.5–6.8	0.1–0.2	4.4–6.7	4.2–7.6	1.5–3.6	0.23–0.56	260–800
<i>Haplic Ferralsol (Santo Antônio de Goiás)</i>							
Forest	4.8	1.2	8.8	0.5	0.2	0.1	1
Experiment	5.7–6.1	0.0–0.1	3.1–4.1	1.3–2.8	0.9–1.2	0.2–0.4	3–9
(B) Particle size distribution							
	Sand (g kg ⁻¹)	Silt (g kg ⁻¹)	Clay (g kg ⁻¹)				
<i>Rhodic Ferralsol</i>							
Forest	63	211	726				
Experiment	40	178	782				
<i>Haplic Ferralsol</i>							
Forest	310	110	580				
Experiment	380	127	493				

mesh sieve for analysis, as was in the same manner for an aliquot of the BS samples.

2.4. Conventional sample analysis

Total C and N concentrations of all samples were measured on finely ground samples (80 mesh) by dry combustion (Nelson and Sommers, 1996; Anonymous, 1999) using a Perkin Elmer 2400 Series II CHNS/O Analyzer (Perkin Elmer Life and Analytical Sciences, Inc., Boston, MA, USA). Coefficient of variation of the method was 3%.

The particle size distribution of the bulk soil samples was determined by densitometry: the sand and clay fractions were separated based on their specific gravity, silt was obtained by deducting sand and clay from the total {silt [g kg^{-1}]=1000–(sand + clay)} (Embrapa, 1997). The parameters describing soil aggregate distribution (soil aggregation indices: Meanweight Diameter—MWD, Mean Geometric Diameter—MGD and Aggregate Stability Index—AS) of the BS samples were calculated using the results obtained by aggregate size fractionation and particle size analysis as follows:

MWD of aggregates (Kemper and Rosenau, 1986)

$$\text{MWD} = \sum_{i=1}^n x_i w_i$$

where w_i =proportion of each aggregate class in relation to the whole, x_i =mean diameter of the classes (mm).

MGD of aggregates (Kemper and Rosenau, 1986)

$$\text{MGD} = \exp \left[\frac{\sum_{i=1}^n w_i \log x_i}{\sum_{i=1}^n w_i} \right]$$

where, w_i =weight of aggregates (g) in a size class with an average diameter x_i .

AS of soils (Castro Filho et al., 1998)

$$\text{AS} = \frac{\text{Weight of the dry sample} - \text{wp25} - \text{sand}}{\text{Weight of the dry sample} - \text{sand}} \times 100$$

where wp25=weight of aggregates <0.25 mm (g), sand=weight of particles between 2.0 and 0.053 mm (g).

2.5. Fourier-transformed diffuse reflectance Mid-IR spectroscopy (DRIFTS)

Samples were scanned in the Mid-IR on a Digilab (Bio-Rad, Randolph, MA) FTS-7000 Fourier Transform

spectrometer equipped with a KBr beam splitter and a DGTS (deuterated glycine trisulfate) detector. Samples were scanned from 4000 to 400 cm^{-1} (2500 to 25,000 nm) at 4 cm^{-1} resolution with 64 co-added scans per spectrum. Scanning was performed using ground, but non-KBr diluted (Reeves, 2003a,b), samples using a Pike Autodiff autosampler/reflectance accessory (Pike Technologies, Madison, WI, USA) with KBr used as the reference standard.

2.6. Near-infrared spectroscopy

Samples were scanned in the near-infrared (NIR) on a Digilab (Bio-Rad, Randolph, MA) FTS-7000 Fourier Transform spectrometer equipped with a quartz beam splitter and an InSb liquid nitrogen cooled detector. Samples were scanned from 9091 to 4000 cm^{-1} (1100–2500 nm) at 4 cm^{-1} resolution with 64 co-added scans per spectrum. Scanning was performed using ground samples using the Pike Autodiff autosampler/reflectance accessory with S used as the reference standard. Samples were scanned as originally ground for reference analyses (to pass the 80 mesh=0.177 mm sieve), no further grinding was done prior to DRIFTS and NIRS analysis.

2.7. Statistical analysis

Summary statistics and correlation analysis were performed using SAS (SAS Institute, 1988) PROC Means and FREQ version 8.

2.8. Chemometrics

Calibration development was carried out using SAS PLS with a custom made program (Reeves and Delwiche, 2003, 2004). All spectra were mean centered and variance scaled. In addition, spectral pre-treatments using first and second gap derivatives with gaps of 4–64 data points with and without multiplicative scatter correction (MSC, Martens et al., 1983) were tested. In all, 22 different spectral pre-treatments were tested for all analytes. Initial testing was performed using different spectral ranges and data point averaging to determine the optimal spectral range to use in the final PLSR calibration development (final calibrations based on average of 4 data points with entire spectral range used for both Mid-IR and NIR spectra). Calibrations were developed using the one-out cross validation procedure with and without an independent test set. Calibrations were also examined using GRAMS PLSPlus V2.1G (Galactic Industries, Salem, NH, USA).

3. Results and discussion

3.1. Sample composition

The elemental composition (C, N) for the bulk soil (BS) samples and for the aggregate size fractions (ASF) samples are shown in Table 2. The particle size distribution and the soil aggregation indices for the BS samples are also shown in Table 2. The range of analyte values, even in the BS samples, was fairly wide providing a good data set for the development of NIR or Mid-IR calibrations. It is worthwhile noting that values for silt were sometimes reported as negative due to the method of computation ($\text{silt} = 1000 - \text{sand} - \text{clay}$). These values represent the range of accuracy of the method in question and converting them to 0 could bias calibration equations, thus they were used as computed. The mean C and N values of the BS samples and of the set of all 700 ASF samples are in the same range. The maximum C and N values however are higher for the set of 700 aggregate size fractions. The reason for this is that under certain circumstances, in the present case especially under the natural forest vegetation, more soil organic matter, and consequently more C and N, is accumulated in the microaggregates (the smallest aggregate size fractions) than in the other size fractions (Madari et al., 2005a).

3.2. Mid-IR and NIR spectra

Shown in Fig. 1 are representative Mid-IR and NIR spectra of the 700 aggregate size fractions. Examination

shows that both the absolute magnitude and range of the Mid-IR absorptions are much greater than those found for the corresponding NIR spectrum. It was because of this that quantitative analysis using DRIFTS spectra was held to be impossible unless samples were diluted with KBr, an expensive and time consuming practice not required for NIRS (Reeves, 2003a,b). The Mid-IR spectrum generally shows more distinctive spectral features than the NIR spectrum. Despite this, with the proper chemometric analysis, NIR spectra can be used to accurately determine the composition of many agricultural products (Roberts et al., 2004; Williams and Norris, 1987, 2001). Fig. 1 shows representative Mid-IR and NIR spectra by location (Londrina and Santo Antônio de Goiás). The two areas have two different soil types with difference in mineralogy that is indicated by the Mid-IR spectra. The predominant clay-mineral in the Rhodic Ferralsol of the Atlantic forest biome (Londrina) was kaolinite. The peaks between 3695 and 3620 cm^{-1} and various peaks below 1100 cm^{-1} are characteristic for kaolinite. There is also indication for the presence of other clay minerals, such as gibbsite (peaks between 3610 and 3395 cm^{-1} , and various peaks below 1200 cm^{-1}) (White and Roth, 1986). X-ray analysis confirmed the presence of these, and other clay minerals like hematite and vermiculite with interlayer hydroxyl-Al in trace amounts (Madari et al., 2005a), but the identification of the two latter ones was not evident in the Mid-IR spectra due to overlapping of absorption bands. The Haplic Ferralsol of the Cerrados biome (Santo Antonio de Goiás) had gibbsite and kaolinite as principal constituents of the mineral matrix, and traces of hematite and vermiculite with interlayer hydroxyl-Al, the latter two being difficult to identify in the Mid-IR spectra. X-ray analysis also confirmed the presence of these clay minerals (unpublished data). Soil organic matter also has characteristic absorption bands in the Mid-IR range (Table 3), however, due to its low concentration in the soil samples ($\leq 89.5 \text{ g kg}^{-1}$), and their overlapping with mineral peaks, most of these could not readily be identified by simple visual evaluation in spectra of bulk soil samples. The small bands around 2920–2930 and 2855 cm^{-1} indicates the presence of organic aliphatic C–H stretchings (Fig. 1). This band is more evident in the spectra of soil samples having higher concentrations of organic carbon. Other organic peaks are overlapping with the mineral peaks. Viscarra Rossel et al. (2006), in a study on the usefulness of Mid-IR, NIR and visible diffuse reflectance spectroscopy examining Partial Least Squares Regression (PLSR) factor loadings weights, showed that frequencies in the Mid-IR range

Table 2
Elemental composition (C, N), particle size distribution, and aggregation indices of the 120 bulk soil and 700 aggregate size fraction samples

Variable/analyte	Mean	Standard deviation	Minimum	Maximum
(g kg ⁻¹)				
<i>120 Bulk soil (bs) samples</i>				
Carbon	18.25	6.44	7.90	48.00
Nitrogen	1.30	1.36	0.04	5.60
Sand	203.22	162.32	28.00	460.00
Silt	145.29	55.59	−102.00	304.00
Clay	651.49	128.65	469.00	851.00
MWD ^a	5.33	2.76	0.65	12.51
MGD ^b	1.11	0.09	0.92	1.31
AS ^c	88.84	8.50	55.51	99.76
<i>700 Aggregate size fraction (ASF) samples</i>				
Carbon	20.63	8.99	9.40	89.50
Nitrogen	1.76	1.03	0.60	8.90

^a Mean weight diameter.

^b Mean geometric diameter.

^c Aggregate stability index.

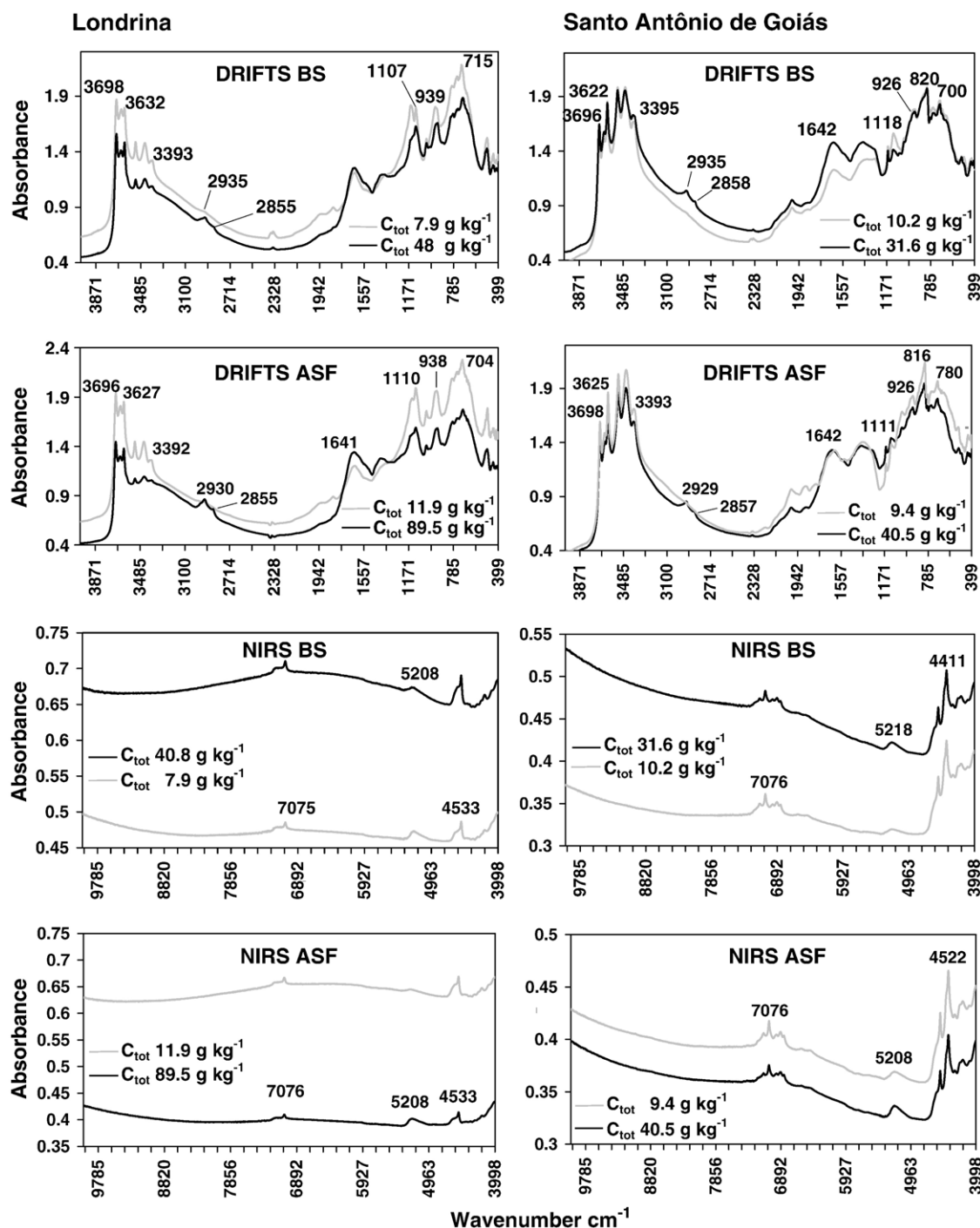


Fig. 1. Representative Mid-IR (DRIFTS) and NIR (NIRS) spectra of the bulk soil (BS) and aggregate size fraction (ASF) samples of the Rhodic Ferralsol (Atlantic forest biome—Londrina) and Haplic Ferralsol (Cerrados biome—Santo Antônio de Goiás) with high and low total C content.

corresponding to the absorption of organic compounds, like organic acids, or acidic functional groups, like alkyl, amide and aromatic groups, were indicators of correlation (showed positive peaks) between organic

carbon concentrations in the bulk soil samples and the Mid-IR spectra. Interfering factors were kaolin and quartz (showed negative peaks). However it seems that certain parts of the spectra have more useful information

Table 3
Absorption bands of carbon in organic bonds in the Mid-IR spectral range

Absorption band, cm^{-1}	Assignments	Overlapping with mineral peaks
3380 ^a	O–H stretching of phenolic OH	OH-stretching frequency for water molecules (Vermiculite)
3400–3300 ^b	O–H stretching (H bonded OH groups), N–H stretching	OH-stretching frequency for water molecules (Halloysite, Montmorillonite, Nontronite, Gibbsite)
3030 ^a	Aromatic C–H stretching	
2940–2900 ^b	Aliphatic C–H stretching	
2600 ^a	O–H stretching of H-bonded –COOH	
1725–1720 ^b	C=O stretching of –COOH and ketones	
1660–1630 ^b	C=O stretching of amide groups (amide I band), quinine C=O and/or C=O of H-bonded conjugated ketones	OH-bending frequency for water molecules (Halloysite, Montmorillonite, Nontronite, Vermiculite)
1620–1600 ^b	Aromatic C=C stretching and/or asymmetric –COO stretching	
1590–1517 ^b	COO– symmetric stretching, N–H deformation + C=N stretching (amide II band)	
1525 ^a	Aromatic C=C stretching	
1460–1450 ^b	Aliphatic C–H	
1400–1390 ^b	OH deformation and C–O stretching of phenolic OH, C–H deformation of CH ₂ and CH ₃ groups, COO– asymmetric stretching	
1350 ^a	Symmetric COO– stretching and/or –CH bending of aliphatics	
1270 ^a	C–OH stretching of phenolic OH	
1280–1200 ^b	C–O stretching and OH deformation of COOH, C–O stretching of aryl ethers	
1225 ^a	C–O stretching and OH deformation of COOH	
1170–950 ^b	C–O stretching of polysaccharides or polysaccharide-like substances	Si–O of silicate impurities (various clay minerals)
1170 ^a	C–OH stretching of aliphatic OH	
1170 ^c	Polysaccharides	
1070 ^a	C–C stretching of aliphatic groups	Si–O of silicate impurities (various clay minerals)
1050 ^c	Polysaccharides	Si–O of silicate impurities (various clay minerals)
830 ^a	Aromatic CH out of plane bending	Nontronite, Muscovite
775 ^a	Aromatic CH out of plane bending	

^a Baes and Bloom (1989).

^b Stevenson (1994).

^c Niemeyer et al. (1992).

for the calibration for a certain analyte; efforts with many sample sets using selected spectral ranges have demonstrated that information exists across the whole spectral range used in the calibrations. Using only parts of the Mid-IR spectra (e.g. leaving out the $<1200 \text{ cm}^{-1}$ range; unpublished data) resulted in less accurate calibrations than using the whole spectra. Even leaving out ranges where no apparent bands were present (e.g. $2500\text{--}2000 \text{ cm}^{-1}$) has been shown to degrade PLSR calibrations.

The shift in overall baseline in the NIR spectra is likely caused by the overall difference in the particle size distribution versus composition of the samples of the two locations (Fig. 2). As it is shown in Table 1, the soil from Londrina has a finer texture compared to the other location, which results in a higher baseline. For most types of samples, smaller particle size results in higher reflectance, e.g. lower absorbances, but for these soils, the higher absorption

coefficients for the clay and silt fraction apparently dominates the particle size effect resulting in higher absorbances for the Londrina samples. The NIR spectra features absorption peaks associated with the bending (7075 cm^{-1}) and stretching (5219 cm^{-1}) of the O–H bonds of free water, and in lattice minerals at around 4523 cm^{-1} . The peak at 4413 cm^{-1} in the spectra of the Cerrado soil (Santo Antônio de Goiás) may indicate the difference in the mineral composition compared to the soil from the Atlantic forest biome (Londrina).

3.3. Calibrations for the bulk soil (BS) samples

Table 4 contains the calibration results using Mid-IR (Table 4a) and NIR (Table 4b) spectral ranges. Calibrations for C, N, sand, clay and location produced R^2 above 0.90 using spectra from either spectral range. It is notable however that for these

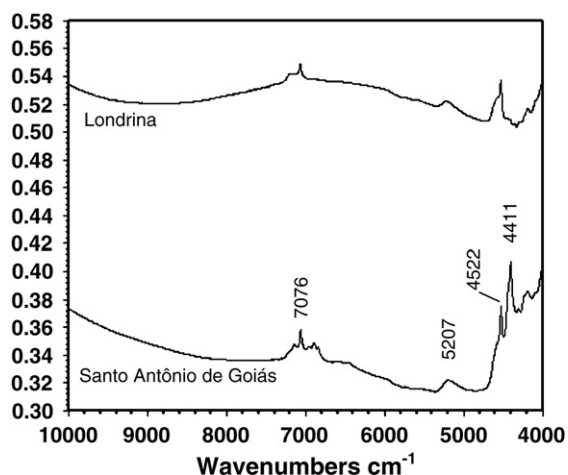


Fig. 2. Average near-infrared spectra of aggregate size fraction (ASF) samples by location.

samples, neither spectral range consistently produced the best calibration.

In the Mid-IR range, the R^2 value was 0.93 and the number of factors for the C calibration model with the lowest RMSD (1.73 g kg^{-1}) was 4. In the NIR the R^2 was 0.90, however, the number of PLS factors for the lowest RMSD (0.721 g kg^{-1}) was 10. In general, the fewer the factors used, the better, as the calibration is more apt to be applicable to new samples. These results for Mid-IR corroborate with those found in the literature (0.95 by [McCarty et al., 2002](#); 0.81–0.95 by [Madari et al., 2005b](#)), however for NIR R^2 values reported elsewhere were a bit lower (0.86 by [McCarty et al., 2002](#); 0.96 by [Reeves et al., 1999](#); 0.74–0.96 by [Madari et al., 2005b](#)) than our findings. Past efforts have shown that calibrations for C are in general better when using Mid-IR spectra ([Reeves et al., 2001](#); [McCarty et al., 2002](#); [Reeves et al., 2002](#)), but, concerning accuracy, that was not the case here. In [Fig. 3A](#) and [C](#) the Mid-IR and NIR calibrations for C are shown, respectively. While the NIR calibration for C show all the data points close to the 1:1 line, the data for C by Mid-IR shows more scatter with even a few samples clearly not being determined as well as the others. Since the same sample was scanned and the same chemistries used, the reason for the poorer performance for C by Mid-IR is not readily explained.

In the Mid-IR range, the R^2 value was 0.99 and the number of factors for the N calibration model with the lowest RMSD (0.148 g kg^{-1}) was 12. In the NIR the R^2 was 0.97, however, the number of PLSR factors for the lowest RMSD (0.233 g kg^{-1}) was 3. The accuracy of the calibration with NIR was a bit higher, but in the

order of magnitude, compared with those found in the literature (0.92 by [Dalal and Henry, 1986](#); 0.94 by [Reeves and McCarty, 2001](#); 0.95 by [Reeves et al., 1999](#)). No comparative results were found in the literature for Mid-IR. Own results, for a heterogeneous sample population ($n=1135$) in terms of soil type and soil texture ([Madari et al., 2005b](#)), showed $R^2=0.95$.

In [Fig. 3B](#) the Mid-IR calibration for N is shown. The Mid-IR calibration for N also show little dispersion of data points from the 1:1 line, such as the NIR calibration for C ([Fig. 3C](#)).

The ability to discern the location of the samples from the spectra was found to be very easy ($R^2=1.00$ by Mid-IR and 0.999 by NIR). Considering the differences in the spectra from the two soils as shown in [Fig 1](#), these results are not surprising. The two locations represent two different soil types with different mineralogy and particle size distribution ([Table 1](#)). It is worthwhile noting that the NIR calibration did not use multiplicative scatter correction (MSC) which is designed to remove baseline effects ([Martens et al., 1983](#)). This indicates

Table 4

Analyte	Derivative	Gap ^a	Scatter Correction	No. of factors ^b	RMSD ^c	R^2
(a) Final calibration results using 120 bulk soil (BS) samples and mid-infrared spectra						
Carbon	2nd	4	MSC	4	1.73	0.93
Nitrogen	1st	4	MSC	12	0.148	0.99
Sand	None	0	MSC	11	15.4	0.99
Silt	None	0	MSC	11	24.7	0.80
Clay	None	0	MSC	11	24.7	0.96
MWD ^d	2nd	8	MSC	5	1.27	0.79
MGD ^e	2nd	8	None	5	0.0432	0.79
AS ^f	2nd	8	None	5	3.83	0.80
Location	1st	4	MSC	13	0.0186	1.00
(b) Final calibration results using 120 bulk soil (BS) samples and near-infrared spectra						
Carbon	2nd	8	MSC ^g	10	0.721	0.99
Nitrogen	2nd	32	MSC	3	0.233	0.97
Hydrogen	1st	16	None	6	2.41	0.87
Sand	1st	8	MSC	5	17.1	0.99
Silt	1st	4	MSC	2	33.5	0.64
Clay	2nd	64	None	3	32.4	0.94
MWD ^a	2nd	8	None	3	1.61	0.66
MGD ^b	2nd	8	None	3	0.0544	0.67
AS ^c	1st	8	None	9	2.41	0.92
Location	1st	16	None	11	0.0249	0.99

^a Number of data points skipped for derivatives.

^b Number of partial least squares factors used in calibration.

^c Rootmean squared deviation.

^d Mean weight diameter.

^e Mean geometric diameter.

^f Aggregate stability index.

^g Multiplicative scatter correction.

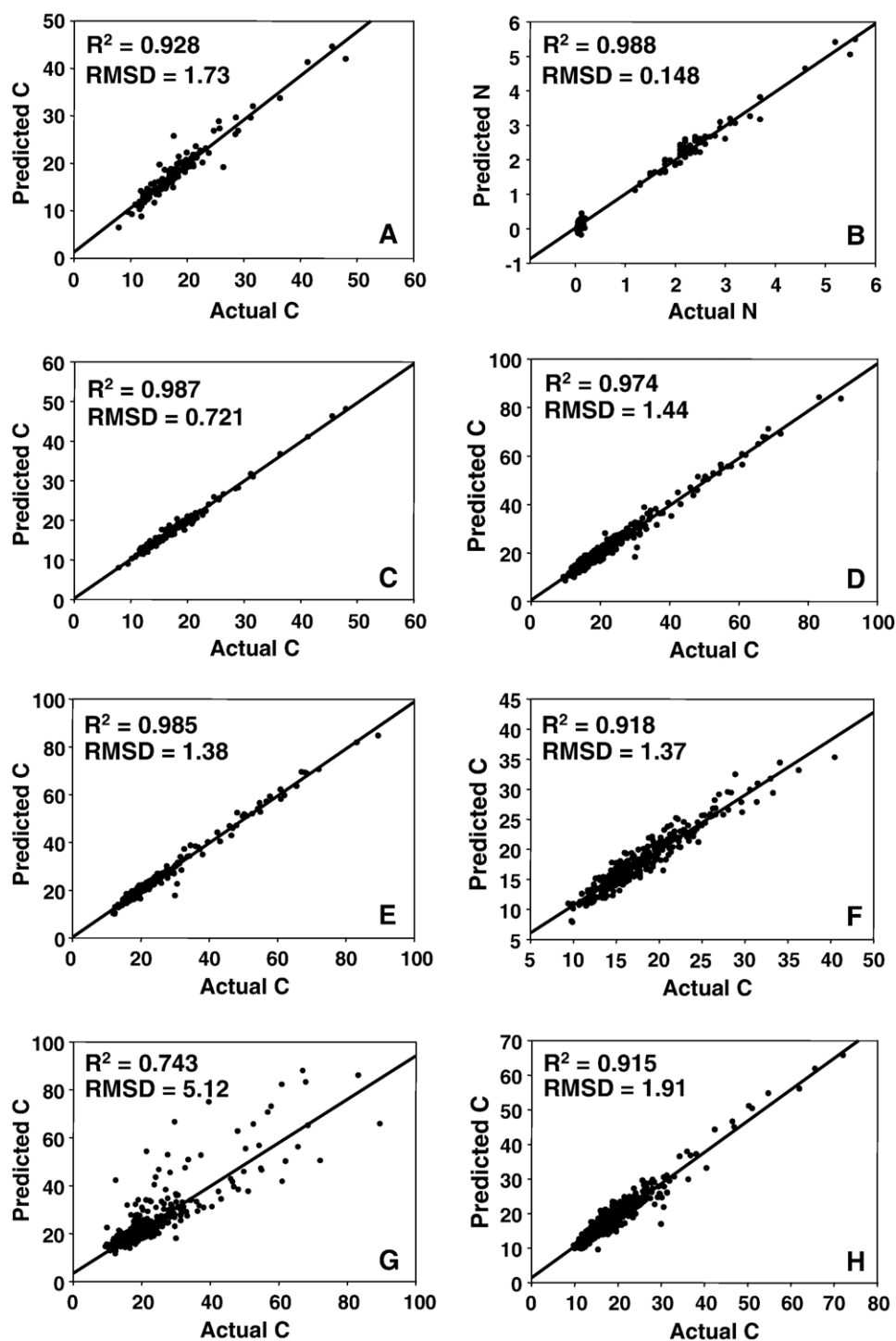


Fig. 3. Mid- and near-infrared calibration curves using PLSR. (A) Mid-infrared calibration for C (g kg^{-1}) using 120 bulk soil (BS) samples. (B) Mid-infrared calibration for N (g kg^{-1}) using 120 bulk soil (BS) samples. (C) Near-infrared calibration for C (g kg^{-1}) using 120 bulk soil (BS) samples. (D) Mid-infrared calibration for C (g kg^{-1}) using 700 aggregate size fraction (ASF) samples. (E) Mid-infrared calibration for C (g kg^{-1}) using aggregate size fraction samples from (ASF) Londrina. (F) Mid-infrared calibration for C (g kg^{-1}) using aggregate size fraction samples (ASF) from Santo Antônio de Goiás. (G) Determination of C (g kg^{-1}) for 700 aggregate size fraction samples (ASF) from calibration developed using 120 bulk soils (BS). (H) Determination of C (g kg^{-1}) for remaining 564 aggregate size fraction (ASF) samples from calibration developed using 120 bulk soil (BS) samples plus 136 of aggregate size fraction samples chosen by spectral diversity.

that the calibration used the overall differences, including those due to physical effects as seen in the average spectra (Fig. 2) for the two ranges, while the Mid-IR calibration did not.

While such differences have been seen in calibrations for sand, silt and clay in other samples (unpublished data), the same was not true here for the calibrations for sand, silt and clay where MSC was used for all calibrations but that for clay in the NIR. The accuracy of the calibration for sand and clay was fairly high, showing R^2 values of 0.99 and 0.96 for sand and clay, respectively, using Mid-IR (number of factors was 11 for both analytes), and 0.99 and 0.94 using NIR (number of factors was 5 and 3 for sand and clay, respectively). The accuracy of the calibrations for silt was lower in both spectral ranges ($R^2=0.80$ for Mid-IR and 0.64 for NIR), but especially in the NIR. The one result found in the literature for sand in the Mid-IR (0.94 by Janik et al., 1998) was similar to our value. No results were found for sand using only the NIR range, some works using combined visible-NIR found R^2 between 0.70 and 0.82 (Chang et al., 2001; Schepherd and Walsh, 2002; Cozzolino and Moron, 2003 in Viscarra Rossel et al., 2006). Comparative results for clay in the Mid-IR in the literature were 0.79 (Janik et al., 1998) and 0.87 (Janik and Skjemstad, 1995), in the NIR 0.56 (multiple regression analysis and not PLSR or PCR; Ben-Dor and Banin, 1995 in Viscarra Rossel et al., 2006) and 0.75 (Islam et al., 2003). Our results for silt corroborate with results in the literature. Janik et al. (1998) obtained $R^2=0.84$ in the Mid-IR, and Chang et al. (2001), Cozzolino and Moron (2003) and Schepherd and Walsh (2002) obtained 0.84, 0.80 and 0.67, respectively, in the visible-NIR range, however the last value (0.67) is, again, a result of multiple regression analysis that seems to perform poorer than PLSR or PCR. In our study the lower accuracy in calibration for silt compared to clay and sand may be the consequence of errors in the reference method for silt determination, which is not a direct measurement of this fraction but is calculated by difference, thus being more prone to inaccuracy of the results.

Madari et al. (2005b) found that the granulometric homogeneity, or in other words the range of particle size distribution within the soil sample population, and also within each sample of the calibration set, affects the accuracy of calibration for total C and organic C both in Mid-IR and NIR, however, NIR proved to be more sensitive to particle size effects than the Mid-IR range. It was shown for total and organic C that using sample populations separated by textural classes improves the accuracy of the calibration compared to a calibration

that used a more heterogeneous population regarding particle size distribution. The more homogeneous the particle size distribution among the samples of the calibration set, the higher accuracy is achieved in the calibration. The effect of the particle size distribution was bigger in the NIR range. NIR spectroscopy performed very well for a very homogenous sample population, even slightly better than Mid-IR, but with increasing heterogeneity among and within the soil samples the accuracy diminished drastically, while the RMSD increased. The particle size distribution had less effect in the Mid-IR range. For the very homogeneous sample population the accuracy of the calibration was slightly lower than using NIR, but with the increase in the heterogeneity of the sample population the accuracy did not diminish drastically and was higher than using NIR. Thus Mid-IR calibrations can be considered more robust than NIR calibrations. This same study also showed that soil type was not a determining factor for establishment of calibration sets. This might be, at least partly, the reason why NIR calibration gave better accuracy for the sample population used in this study, as the samples are from two different areas with different soil types and texture, however, within one area the textural class of the soil samples was the same, very clayey in Londrina, and clayey in Santo Antonio de Goiás (Table 1).

Several parameters describing aggregate size distribution (soil aggregation indices: MWD, MGD and AS) were also examined. The calibrations found for these indices resulted in R^2 between 0.79 and 0.80 using Mid-IR and 0.66 and 0.92 using NIR. In general Mid-IR gave a better approximation of the calculated values. Considering that the aggregation indices are not directly measured, but calculated values, R^2 around 0.80, from a practical point of view, can be considered reasonable. Soil aggregation is a complex phenomenon in which a number of factors are involved. Some of these are the mineralogical composition of the soil, particle size distribution of the soil, soil organic matter quantity and quality, soil biological parameters, vegetation, land use, etc. The infrared spectrum reflects most of these factors. The standard way of determination of these indices is the result of a long and laborious laboratory procedure that itself holds various opportunities for error inclusion. As the calibration is obtained using values determined in such a way, it could not be better than the original data. Considering all this, a calibration with an R^2 close to 0.80 can provide a reasonable estimate of soil aggregation properties, and provide important information on soil structure.

3.4. Calibrations for aggregate size fractions

In Table 5, the results obtained using spectra of the 700 aggregate size fractions are presented. For these calibrations, the results using Mid-IR spectra were slightly better for all analytes. The calibrations for all the examined analytes (C, N) including location were quite good regardless the spectral range used. Fig. 3D demonstrates the calibration made for C by Mid-IR. The fact that location was so readily discriminated even for the soil fractions shows that the difference in the soils from the two locations was at a fundamental level. This is not surprising since, as mentioned before, the two locations have soils with different mineralogy and different particle size distribution and these properties are readily reflected in the infrared spectrum.

As the samples from the two locations appeared to have differences at a fundamental level, calibrations were tested using samples from a single location. These results are shown in Table 6 and Figs. 3E and F. As shown, calibrations for C and N were very similar using either spectral range, but were much better for samples from Londrina. Two possible explanations for the higher accuracy of the calibration for the Londrina samples are the following. Table 1B shows that the range of C and N concentrations for the Londrina samples was larger, which can produce better R^2 due to the nature of regression analysis. Another reason may be in the difference in the heterogeneity of the particle size distribution among the samples within each sample populations (Londrina and Santo Antonio de Goiás), as mentioned above. The Londrina soil, having a very clayey texture, it consists of almost 80% clay-size particles with a small contribution of sand- and silt-size

Table 5
Final calibration results using 700 aggregate size fraction (ASF) samples and mid- and near-infrared spectra

Analyte	Derivative	Gap ^a	Scatter correction	No. of factors ^b	RMSD ^c	R^2
<i>Mid-infrared spectral calibrations</i>						
Carbon	2nd	16	MSC ^d	12	1.44	0.97
Nitrogen	1st	4	MSC	12	0.174	0.97
Location	1st	4	MSC	15	0.0216	1.00
<i>Near-infrared spectral calibrations</i>						
Carbon	1st	4	MSC	10	1.78	0.96
Nitrogen	1st	4	MSC	9	0.188	0.97
Location	2nd	64	MSC	14	0.0397	0.99

^a Number of datapoints skipped for derivatives.

^b Number of Partial Least Squares Factors used in calibration.

^c Rootmean Squared Deviation.

^d Multiplicative Scatter Correction.

Table 6

Final calibration results using 700 aggregate size fraction samples split by location

Analyte	Londrina samples		Santo Antônio de Goiás Samples	
	RMSD ^a	R^2	RMSD ^a	R^2
<i>Mid-infrared spectral calibrations</i>				
Carbon	1.380	0.99	1.370	0.92
Nitrogen	0.188	0.98	0.142	0.82
<i>Near-infrared spectral calibrations</i>				
Carbon	1.22	0.99	1.47	0.91
Nitrogen	0.174	0.98	0.131	0.84

^a Rootmean Squared Deviation.

particles. The Santo Antonio de Goiás soil has clayey texture, thus has lower contribution of the clay-size particles in its matrix, and higher proportion of the sand- and silt-size particles, that makes every one sample in the group granulometrically more heterogeneous than in the case of the Londrina soil. For this, while for the Londrina samples both spectral ranges performed very well ($R^2=0.99$ and 0.99 using Mid-IR and NIR, respectively), for the Santo Antonio de Goiás samples using either spectral range resulted in lower accuracy in calibration, with Mid-IR being slightly better for C (Table 6). This corroborates with the above mentioned particle size distribution effect, however only for C, for N it was not the case.

3.5. Calibration robusticity

While the results presented indicate that calibrations for C, N and perhaps other analytes of interest should be feasible for soil fractions, the question remains whether a calibration can be developed and then used on new samples not previously seen (whether it is sufficiently robust). This issue is addressed in Tables 7 and 8 and Figs. 3G and H. In Table 7, efforts are shown to determine the C and N of ASF samples using calibrations developed using the BS samples, and calibrations developed using the BS samples and increasing numbers of the ASF samples chosen on the basis of their spectral diversity. Since a common hypothesis of calibration development is that sample composition is related to spectral information, adding the most diverse spectra should enable a calibration to better fit a more diverse set of samples.

Results showed that calibrations (Mid-IR and NIR) developed using only the BS samples resulted in relatively poor R^2 determining C or N in the ASF samples that were obtained by fractionating the BS

Table 7

Predicted results for aggregate size fraction (ASF) samples using calibrations derived from the 120 bulk soil (BS) samples with and without adding ASF samples to increase sample diversity

Analyte	Mid-infrared spectra		Near-infrared spectra	
	RMSD ^a	R ²	RMSD ^a	R ²
<i>Using calibrations derived from set of 120 BS samples</i>				
Carbon	5.120	0.74	6.130	0.58
Nitrogen	1.000	0.62	0.935	0.63
<i>Using calibrations derived from set of 120 BS plus 35 ASF samples</i>				
Carbon	2.400	0.90	2.840	0.87
Nitrogen	0.594	0.72	0.773	0.58
<i>Using calibrations derived from set of 120 BS plus 70 ASF samples</i>				
Carbon	2.700	0.87	2.920	0.84
Nitrogen	0.355	0.88	0.490	0.79
<i>Using calibrations derived from set of 120 BS plus 105 ASF samples</i>				
Carbon	2.280	0.89	2.970	0.80
Nitrogen	0.285	0.89	0.710	0.62
<i>Using calibrations derived from set of 120 BS plus 136 ASF samples</i>				
Carbon	1.910	0.92	2.730	0.82
Nitrogen	0.308	0.87	0.401	0.75

^a Rootmean Squared Deviation.

samples by aggregate size (Table 7 and Fig. 3G). It means that the two sample populations, BS and AFS, are very different. It may be expected that a model developed for a “parent” sample population can be applied to the derived sample population. However, by

fractionating bulk soil in aggregate fractions, in terms of soil organic matter, functionally, and therefore compositionally, very different groups could be created. For example, the range of C and N concentration of the samples of the BS population (7.9–48.0 and 0.04 and 5.60 g kg⁻¹ for C and N, respectively) was amplified in the ASF sample population (9.4–89.5 and 0.6–8.9 g kg⁻¹ for C and N, respectively). Besides this there is qualitative difference in the organic matter in the different aggregate size fractions (Six et al., 2000). We do not have information whether qualitative change occurred in soil organic matter during the fractionation process, for example diminution of soluble fractions of C and especially N, however, adding only 35 samples of the 700 ASF (5% of total set of 700) greatly improved the results for C (R^2 increased from 0.743 to 0.904, and RMSD decreased from 6.13 to 2.84). The results for adding 136 (~20% most diverse of the 700 ASF) samples are shown for C in Fig. 3H. The results using less than 20% of the total number of the ASF samples are quite good with a few samples appearing as outliers. The fact that the results did not get better in an orderly fashion with the addition of more samples and that the results for N never approached those achieved for C indicates that perhaps there is too much difference between the BS and ASF samples for the best calibration to be developed. However, the results do indicate that at least for C, a calibration

Table 8

Average calibration and validation results derived from 25 calibrations developed using 20% of total set of 700 aggregate size fraction (ASF) samples as the calibration set and the remaining 80% as the validation set

Criteria	Mid-infrared calibrations				Near-infrared calibrations			
	Mean	Minimum	Maximum	Covariance	Mean	Minimum	Maximum	Covariance
<i>Carbon</i>								
CAL- R^{2a}	0.978	0.940	0.993	1.138	0.962	0.914	0.982	1.54
CAL-RMSD ^b	1.200	0.878	2.014	22.500	1.760	1.260	2.590	19.60
VAL- R^{2c}	0.947	0.928	0.959	0.832	0.907	0.859	0.924	1.81
VAL-RMSD ^d	2.150	1.871	2.695	8.461	2.720	2.460	3.410	1.54
No. of factors ^e	9.920	5.000	13.000	24.200	7.280	5.000	11.000	20.00
<i>Nitrogen</i>								
CAL- R^{2a}	0.961	0.920	0.986	2.068	0.970	0.907	0.995	2.27
CAL-RMSD ^b	0.180	0.121	0.260	21.500	0.170	0.073	0.315	36.00
VAL- R^{2c}	0.942	0.930	0.954	0.795	0.917	0.870	0.938	1.61
VAL-RMSD ^d	0.259	0.288	0.324	9.280	0.298	0.265	0.372	8.55
No. of factors ^e	9.520	3.000	13.000	36.900	7.360	4.000	13.000	35.30

^a Calibration set R^2 .

^b Calibration root mean squared deviation.

^c Validation set R^2 .

^d Validation root mean squared deviation.

^e Number of partial least squares factors used in calibration.

available for BS samples could be used along with some ASF sample spectra to get a quick estimate of the C values for a larger set of soil fractions.

The results in Table 8 were derived by randomly using 20% of the ASF samples (140) to develop a calibration which was then used to determine the results for the remaining 80% (560). This was done 25 times and the best results shown. The results demonstrate that it is possible to use only 20% of the available samples to develop a calibration and determine the remaining samples with a high degree of accuracy, with Mid-IR based calibrations clearly being more robust than their NIR counterparts.

4. Conclusions

The application of Fourier-transformed diffuse reflectance mid-infrared spectroscopy (DRIFTS) and near-infrared spectroscopy (NIRS) was tested for the quantification of total soil C and N, particle size distribution (sand, silt, clay), and for the rapid estimation of three indices that describe soil aggregate distribution. The relevance of this study lays in the necessity of analytical techniques that are able to quantify soil compositional parameters in a rapid and cost effective way.

In this investigation it was shown that both DRIFTS and NIRS when combined with chemometric methods have great potential to quantify total C, N, sand and clay in soil samples. It was also shown that these techniques could also be calibrated to estimate parameters such as soil aggregation indices, which are not directly measurable by other means.

It was shown that DRIFTS calibrations were sufficiently robust to estimate the C content of a “P” sample population using the calibration made for another but similar “R” sample population if some of the members of the P sample population are included in the calibration (max. $R^2=0.91$). Similar calibrations for N were slightly less accurate (max. $R^2=0.89$ using DRIFTS).

To achieve better calibrations, it is advisable to perform the calibration using a representative sub-population of the target sample population. In this way calibrations with an average $R^2=0.98$ were obtained using DRIFTS and $R^2=0.96$ using NIRS for C, and average calibrations for N using DRIFTS resulted in $R^2=0.96$, and using NIRS $R^2=0.97$. It can be concluded therefore that for C calibrations both DRIFTS and NIRS can be successful, however DRIFTS appears to be generally more accurate and robust. For N also both techniques were successful, but NIRS produced slightly better results.

Very good calibrations were achieved for the sand and clay fraction of the soil. DRIFTS gave slightly better results ($R^2=0.99$ for sand and $R^2=0.96$ for clay) than NIRS ($R^2=0.99$ for sand and $R^2=0.94$ for clay). The robusticity of the calibration could not be checked for these analytes.

This study seems to confirm that soil type in itself does not effect calibrations for total C concentrations, but the textural diversity within the sample population used for calibration influences it, NIRS being more sensitive to this particle size effect.

As an overall conclusion, it can be stated that DRIFTS and NIRS in this study were successfully applied to predict the directly measured/measurable soil parameters and can be considered as promising potential techniques for rapid and cost effective sample analysis for various analytes, including soil physical parameters. It is of great importance especially when large number of samples has to be analyzed. In these cases the use of calibrations of even slightly lower accuracy based on these spectroscopic techniques can pay off concerning time and cost effectiveness, not mentioning the advantage of being able to count with a larger and thus more representative sample population for characterization of natural and agricultural ecosystems. It is however worthwhile mentioning that the accuracy of this technique depends on the accuracy of the standard analytical method that is used to calibrate the spectroscopic technique, and, consequently, the spectroscopic method can not provide a more accurate estimation of the analytes, but can provide estimates in a more time and cost effective way with potential cost reductions of 80–90%. Another important advantage of spectroscopic method is their potential field, real-time, applications.

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